

Quasi-2D superconductivity and Fermi-liquid behavior in bulk CaC_6

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The intercalated graphite superconductor CaC_6 with $T_c \sim 11.5$ K has been synthesized and characterized with magnetoresistance measurements. Above the transition, the inter-plane resistivity follows a T^2 dependence up to 50 K, indicative of Fermi liquid behavior. Above 50 K, the data can be fit to the Bloch-Grüneisen model providing a Debye temperature of $\theta_D = 263$ K. By using McMillan formula, we estimate the electron-phonon coupling constant to be $\lambda = 0.85$ which places this material in the intermediate-coupling regime. The angular dependence of the upper critical field parallel and perpendicular to the superconducting planes suggests that this material is a quasi-2D superconductor. All of these measurements are consistent with BCS-like superconductivity.

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Despite the observation of superconductivity in graphite intercalation compounds (GICs) over four decades ago, little progress has been made to significantly raise the transition temperature T_c in this class of materials.^{1,2,3,4} Current theories support a model in which T_c increases with increased charge transfer from the intercalant to the graphene layers. However, some members of this series seem to contradict this view. For example, in LiC_6 , the charge transfer is larger than that of KC_8 , but there is no evidence of superconductivity in LiC_6 .⁵ The application of high pressure also has been used to raise the critical temperature, although in many cases opposite phenomena is observed, except in the case of KC_8 which successfully increases the critical temperature up to 1.5 K in 13 kbar ($T_c = 0.15$ K in ambient pressure). From a theoretical approach, superconductivity in GIC is an interesting problem since the constituent elements are not superconducting alone. Recent works have attacked this problem from the view of band structure calculations.^{6,7,8} It is the general consensus of the community that finely tuned electron-phonon interactions gives rise to BCS-like superconductivity in GICs, which limits the maximum value of T_c . However, recent interest in low-dimensional materials such as MgB_2 , a BCS superconductor with a very high transition temperature $T_c = 39$ K,⁹ has reinvigorated this field and the search for new materials with finely tuned properties. The discovery of relatively high T_c s in materials such as YbC_6 and CaC_6 (8 K and 11.5 K respectively)^{10,11} provides an even further impetus for the understanding of BCS-like phenomena in low dimensional structures.

This paper details the extensive upper critical field magnetoresistivity measurements on the new GIC superconductor CaC_6 . The results of these experiments include: (1) The H_{c2} values are determined for applied magnetic fields parallel and perpendicular to the graphite planes. (2) The resistivity as a function of temperature is fit to several different models. Fermi-liquid behavior is noted below 50 K (T^2 dependence), and above 50 K, the best fit to the data is with a Bloch-Grüneisen model. The extracted coupling constant λ agrees with density func-

tional theory calculations. (3) Through the dependence of the upper critical field as a function of field direction, we have determined that CaC_6 is a quasi-2D superconductor.

CaC_6 samples were prepared using highly-oriented pyrolytic graphite with a liquid-solid reaction extreme.¹¹ A lithium-calcium alloy (of the ratio 3:1) was prepared inside of an argon glove box at 220 degrees C, and thin sheets of pristine graphite were inserted. The entire sample mixture was sealed in a stainless-steel reaction container, and then placed on a hot plate at 350 degrees for 10 days. The final samples were extracted from the molten solution inside of the glove box, and only very thin samples which exhibited shiny metallic surfaces were used for the measurements. The transition temperature of 11.5 K was confirmed with DC susceptibility measurements (Quantum Design SQUID) in a field of 50 G applied parallel to the ab-plane. From the saturation of the diamagnetic signal, the samples used for the remaining measurements were estimated to have a volume fraction of over 95 percent of the superconducting phase. The resistivity data were measured using a conventional four-probe method with current applied along c-axis. The size of a single crystal is 1.5 mm \times 1 mm \times 0.2 mm. The resistivity measurements were completed in a He-flow cryostat at the NHMFL, Tallahassee.

A few theoretical models have been developed to explain the temperature dependence of the inter-plane resistivity in GICs. One of these is inspired by the theory of variable-range hopping in parallel with band conduction.¹² This model can be well applied for acceptor GICs. Another model proposed by Sugihara¹³ suggests the importance of impurity and phonon-assisted hopping that has a linear dependence on temperature. We estimate the conductivity (along c-axis) in this sample to be $8.7 \times 10^3 \Omega^{-1}\text{cm}^{-1}$, which is a typical value for donor GICs. Thus, we use the latter model in addition with the theory of thermal scattering of charge carriers in a single band, which has been used for many GICs¹⁴ to analyze the temperature dependence of the inter-plane resistivity above 50 K, as shown in figure 1. According

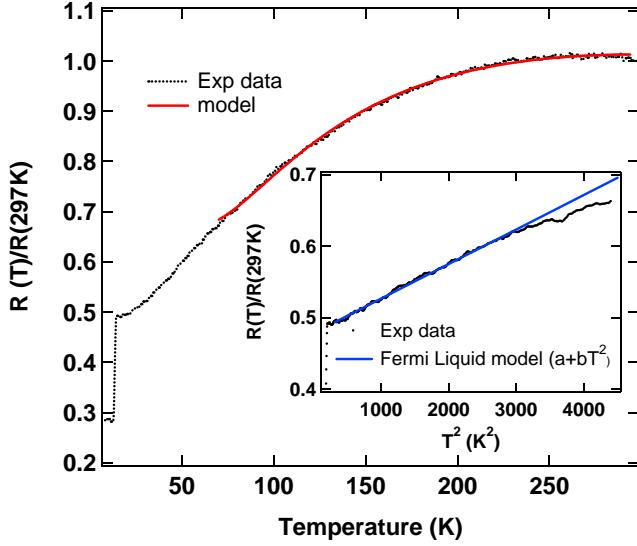


FIG. 1: Inter-plane resistivity as a function of temperature normalized to 297 K. The inset shows a clear T^2 dependence below 50 K. Above 50 K, the data is fit to the Bloch-Grüneisen model as outlined in the text.

to this model the total resistivity can be written as,

$$\rho(T) = \rho_0 + AT + BT^5 \int_0^{\theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx \quad (1)$$

where θ_D is the Debye temperature. The first term in Eq.1 is a temperature-independent constant, the second term is related to the phonon-assisted hopping and the last term is related to the electron-phonon scattering, also known as the Bloch-Grüneisen formula. This parameter from our fit is found to be 263(1) K, which is in good agreement with other GICs fit with this model (which range from 200 K - 300 K).^{3,15,16} The inset shows the normalized resistivity at lower temperatures and as a function of T^2 . The clear dependence on T^2 is strong evidence for Fermi-liquid behavior for CaC_6 .

Using this characteristic temperature, one can estimate the electron-phonon coupling parameter using the McMillan¹⁷ equation:

$$\lambda = \frac{\mu \ln(\frac{1.45T_C}{\theta_D}) - 1.04}{1.04 + \ln(\frac{1.45T_C}{\theta_D})(1 - 0.62\mu)} \quad (2)$$

where μ is the screened potential and λ is the electron-phonon coupling parameter. Using the μ parameter of 0.1, a value of λ of 0.85 is obtained. This is in excellent agreement with theoretical predictions using density functional theory (0.83).¹⁸ The high value of λ indicates that this material is in the intermediate-coupling regime. Other superconducting GICs typically have much lower values for $\lambda = 0.2 - 0.5$.^{3,19,20} The high value of λ certainly plays a role in the anomalously high T_c compared to other intercalated graphite compounds.

The inter-plane resistivity measurements as a function of applied field are shown in the inset of figure 2. The

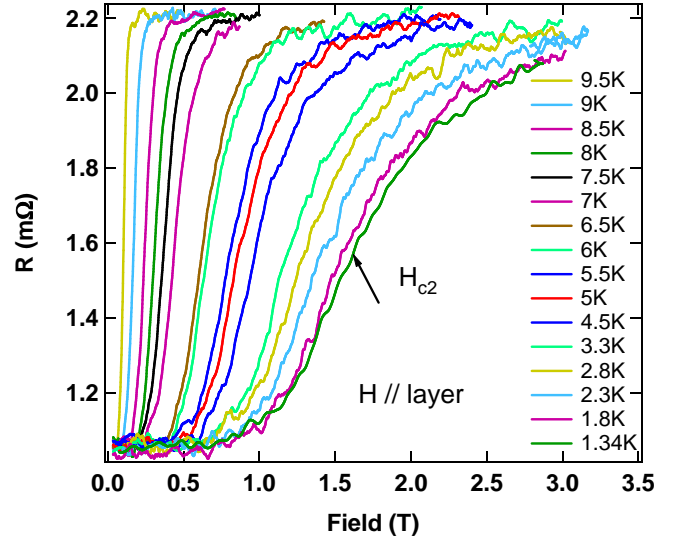


FIG. 2: The inter-plane resistivity plots as a function of applied field which were used to extract the critical field as the midpoint of the resistivity drop at the transition.

midpoint of the gradient of the resistivity drop was used to estimate the transition temperature H_{c2} perpendicular and parallel to the ab -plane. The values of H_{c2} agree with susceptibility measurements for CaC_6 in the previous work.¹¹ As seen in other GIC compounds,^{20,21,22} a linear dependence of H_{c2} on temperature is observed, as shown in figure 3. This linear dependence indicates that the anisotropy is temperature independent. Moreover, this also suggests that there is no evidence of dimensional cross-over, at least down to 1.4 K. The critical field in the anisotropic Ginzburg-Landau theory can be written as²³

$$H_{C2}^i = \frac{\Phi_0}{2\pi\xi_j(T)\xi_k(T)} = \frac{\Phi_0}{2\pi\xi_j(0)\xi_k(0)} \left(1 - \frac{T}{T_c}\right) \quad (3)$$

where $\Phi_0 = h/2e = 2.07 \times 10^{-15} \text{ Tm}^2$ is the flux quantum and ξ is the coherence length. The indices i, j and k represent the cyclic permutation of the directions a, b and c . By applying Eq. 3 for our data in figure 3, we obtain the correlation lengths $\xi_{\perp}(0)$ and $\xi_{\parallel}(0)$ to be 6.0 nm and 29.7 nm, which can be compared to DC susceptibility measurements of 13.0 nm and 35.0 nm.¹¹ It was originally surmised that this was an anisotropic 3D superconductor, but the c -axis correlation length has been over-estimated in the previous work.¹¹ Since the c -axis lattice parameter is 1.357 nm due to the stacking sequence of Ca atoms, it is perhaps not unusual that this material may have quasi-2D superconductivity.

The angular dependence of the critical field in CaC_6 , which has a higher critical field parallel to the ab -plane than that of the perpendicular direction, is shown in Figure 3. Note that the 90 degree position corresponds to an applied field parallel to the ab -plane. We compare this behavior with the two following models. The first model is using anisotropic Ginzburg-Landau (GL) theory, which

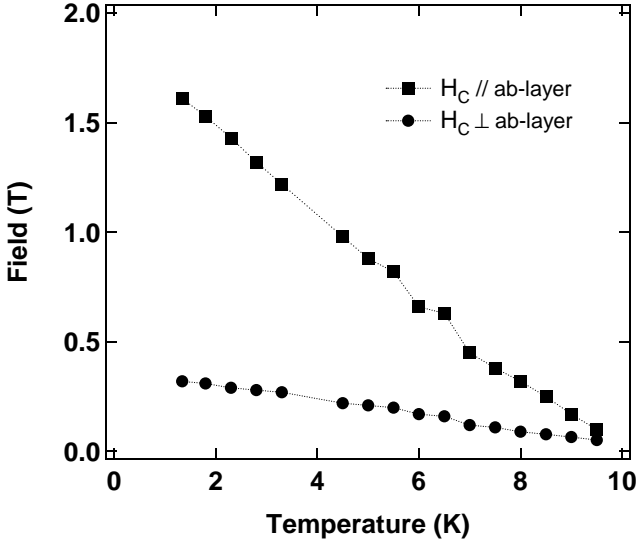


FIG. 3: Upper critical field H_{c2} for fields perpendicular and parallel to ab-plane as a function of temperature

is valid when the interlayer spacing is much smaller than the c-direction coherence length. In this case, the upper critical field depends on the angle between the layers and the applied field through²⁴

$$\left[\frac{H_{c2}(\theta)\cos(\theta)}{H_{c2\perp}} \right]^2 + \left[\frac{H_{c2}(\theta)\sin(\theta)}{H_{c2//}} \right]^2 = 1 \quad (4)$$

where the upper critical fields for directions parallel and perpendicular to the ab-plane are $H_{c2//}$ and $H_{c2\perp}$. The second model is based on Lawrence-Doniach (LD) theory, which assumes that there is a weak coupling between the superconducting layers in the two-dimensional (2D) limit. In this case, the angular dependence of the layers is found to be:²⁵

$$\left| \frac{H_{c2}(\theta)\cos(\theta)}{H_{c2\perp}} \right| + \left[\frac{H_{c2}(\theta)\sin(\theta)}{H_{c2//}} \right]^2 = 1 \quad (5)$$

This model has been used to describe the angular dependence of the magnetoresistivity for thin films, and for two-dimensional superconductors in general.²⁶ The main feature in GL model is a rounded shape at 90 degrees, while the LD model produces a sharp cusp at 90 degrees. We fit these two models to our data, as shown in figure 4. The Lawrence-Doniach model gives a better fit than that of Ginzburg-Landau model. Furthermore, a cusp-like feature at 90 degrees, which is a signature of the LD-model, is also observed as shown in the inset of figure 4. We fit the data at low temperatures (1.4 K) using these two models. Note that the Lawrence-Doniach model still gives a better fit up to 180 degrees, and the cusp-like is less pronounced. We confirmed this 2D-model for another measurement in a helium-3 system at a temperature of 0.5 K (data is not shown).

One theory that has been used to understand the mechanism of superconductivity in GICs is that pro-

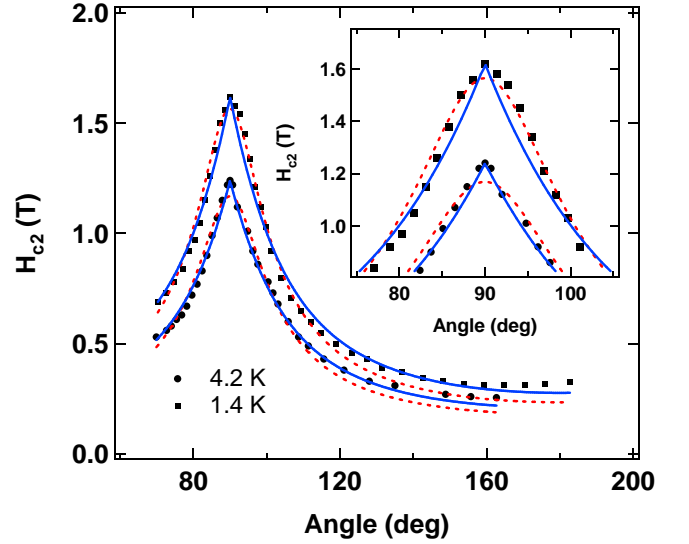


FIG. 4: Angular dependence of the upper critical field for 1.4 K and 4.2 K. The solid and dashed lines indicate the fitting curves for LD-model and GL-model, respectively.

posed by Jishi.⁶ In this model, it has been presumed that the superconductivity arises from a coupling between the graphene π bands and the intercalant layer s band. Moreover, the linear dependence of critical field also can be explained quantitatively using this model.²⁷ However, this model is valid only in the weak-coupling regime ($\lambda < 0.4$) and our results indicate that CaC_6 is in intermediate coupling regime ($\lambda < 0.85$). Although other models have been proposed to explain the origin of superconductivity in CaC_6 recently,^{8,18,28} there is no quantitative explanation for the linear dependence of the upper critical field.

The observation of a T^2 dependence of the resistivity is consistent with the conjecture that CaC_6 is a BCS-like superconductor. Recent penetration depth measurements²⁹ and heat capacity experiments³⁰ have showed that the superconductivity is indeed s-wave and BCS-like, respectively. Fermi-liquid theory provides a natural avenue to produce BCS superconductivity. It is surprising that such a large transition temperature of 11.5 K is observed, but given the large coupling parameter deduced from our measurements (and, recently through specific heat experiments), it is likely that the origin of the superconductivity is through finely tuned electron-phonon interactions.

In conclusion, extensive resistivity measurements on the new GIC CaC_6 have revealed several key features of this new superconductor: (1) There is a prominent anisotropy in the upper critical field parallel and perpendicular to the layers, (2) there is a Fermi-liquid regime below 50 K and (3) this GIC is a quasi-2D superconductor. BCS-theory gives a value for the coupling constant which is in the intermediate regime, which is in agreement with recent specific heat measurements.³⁰ All of these observations are consistent with the view that CaC_6 is a

BCS-superconductor with finely tuned electron-phonon interactions which gives rise to the large T_c .

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